retical amount of Bu_3SnCl was formed after 24 hr. A run under oxygen proceeded to only *ca.* 15% conversion in 4 hr and *ca.* 35% in 24 hr.

Reduction of Phenyl Benzyl N-Chloroketimine (2) with Bu_3SnH. A. 130–131°.—A solution of 30.3 mg (0.206 mmol) of *o*-dichlorobenzene in 10 ml of chlorobenzene was flushed with nitrogen and heated to reflux. Separate solutions of 227 mg (0.99 mmol) of N-chlorimine 2 in 5 ml of chlorobenzene and 303 mg (1.04 mmol) of Bu_3SnH in 5 ml of chlorobenzene were added under nitrogen at the same rate from motor-driven syringes over a 5-hr period. A cold trap was placed in the system to trap any volatile material which escaped the reflux condenser. Glpc analysis of aliquots indicated that toluene was formed essentially as fast as the reagents were added. At the end of the addition period, titration of an aliquot indicated 1.10 mmol of Bu_3SnCl formed. Glpc analysis revealed 76% toluene and 90–100% benzonitrile formed.

B. 35–40°.—To a solution of 235 mg (1.03 mmol) of N-chloroketimine 2 and 20 μl (0.196 mmol) of chlorobenzene in 15 ml of benzene was added a solution of 308 mg (1.06 mmol) of Bu_3SnH in 5 ml of benzene from a motor-driven syringe over 5 hr under N_2. The solution was irradiated throughout with a 275-W sun lamp at *ca.* 6 in., and the temperature was maintained at 35–40° by cooling with an air stream. Titration of an aliquot after 3-ml addition (0.64 mmol Bu_3SnH added) showed that 0.41 mmol of Bu_3SnCl had formed. At the end of the addition, 0.70 mmol had formed, and, after 1.3 hr additional, 0.75 mmol. Glpc analysis then showed 4% toluene, 8% benzyl chloride (apparently from inlet decomposition of residual 2), and 15% benzonitrile, by comparison to the chlorobenzene internal standard. Addition of dry hydrogen chloride to the residual reaction mixture and chilling overnight gave a solid, mp 215–216°, whose infrared spectrum agreed with that of phenyl benzyl ketimine hydrochloride; the yield corrected for the aliquots removed for titration was 0.57 mmol, *at least* one-half of which must have been derived from ketimine in the reaction mixture rather than residual 2 based on the final titration for Bu_3SnCl.

Registry No.—1, 7699-76-5; 2, 20453-02-5; 3, 20452-77-1; 1-phenyl-3-nonanol, 20452-78-2; 12, 20452 79-3; Bu_3SnH, 688-73-3.

Autoxidation of 1-Octene with *t*-Butyl Hydroperoxide and Chromium(III) Acetylacetonate. I. Kinetics

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The system chromium(III) acetylacetonate–*t*-butyl hydroperoxide has been used to initiate autoxidation of 1-octene in 1-chlorooctane solvent in the temperature range 0–60°. Emperical kinetic equations are presented based upon spectrophotometrically determined disappearance rates of chromium(III) acetylacetonate, titrimetrically determined *t*-butyl hydroperoxide decomposition rates, and oxygen absorption data. Activation parameters for the kinetic data have been calculated. The data are interpreted in terms of two superimposed chain reactions, one involving peroxide decomposition through chromium complexes, the other involving chain autoxidation of the 1-octene. Products of the autoxidation are compared with azo-initiated olefin autoxidation products.

Recently, metal acetylacetonates have been studied in terms of their ability to promote olefin epoxidation,[2,3] amine oxidation,[4] styrene polymerization,[5] and autoxidation[6] in the presence of hydroperoxide. This paper and subsequent ones[7] describe in some detail the use of chromium(III) acetylacetonate and *t*-butyl hydroperoxide as an autoxidation initiator for 1-octene. Reaction mixtures from the 1-octene autoxidation have been chromatographed and compared with azo-initiated autoxidation.[8] The effects of solvents and free-radical inhibitors on the reaction are described in part II.[7]

Experimental Section

Chemicals.—The chemicals for these experiments have been described previously.[6]

Kinetics.—Oxygen absorption measurements and *t*-butyl hydroperoxide decomposition studies for these experiments are as previously described.[6] The rate of chromium(III) acetylactonate disappearance was measured by observing the disappearance of the absorption peak at 336 mμ (ε 15,500 l./mol-cm).[9] Samples for analysis were taken from the same evacuated tubes as for *t*-butyl hydroperoxide decomposition studies and diluted in chlorobenzene. Measurements were done on a Cary Model 14 or a Perkin-Elmer Model 202 spectrophotometer. The reference cell contained chlorobenzene. It was observed that the presence of *t*-butyl hydroperoxide in chromium(III) acetylacetonate solutions caused deviations in Beer's law plots of absorbance *vs.* concentration. Corrections were made either by including *t*-butyl hydroperoxide in the reference cell or from calibration curves of absorption *vs. t*-butyl hydroperoxide concentration.

Rates in all cases were taken from initial portions of the kinetic curves. Rates of autoxidation and *t*-butyl hydroperoxide decomposition showed considerable curvature (lowering) after the initial portions. Chromium(III) acetylacetonate disappearance was linear. The reproducibility of duplicate rate measurements was *ca.* ±5% for chromium(III) acetylacetonate disappearance, *ca.* ±3% for autoxidation, and *ca.* ±6% for *t*-butyl hydroperoxide decomposition.

Product Analysis.—Product analysis was done by vapor phase chromatography on a Perkin-Elmer Model 154 gas chromatograph using a glass 88-in. Carbowax 20M column, helium pressure 10 psi, column temperature 150°, block temperature 74°. Retention times of products from previously described systems were used to correlate products from this work. Retention times of significant compounds are given in Table I for the above column conditions.

Preparation of 3-*t*-Butylperoxy-1-octene, 1-*t*-Butylperoxy-3-octene, and 3-Octenal.—Following the method of Kharasch and Fono[10] 0.033 g of cuprous chloride, 10 ml of 1-octene, and 2 ml of *t*-butyl hydroperoxide were mixed under nitrogen for *ca.* 5 hr at 60–70°. Four products peaks were observed gas chromatographically. Products of long retention time were assigned to the dialkyl peroxides, *t*-butyl alcohol was identified by comparison to an authentic sample, and octenal was assigned the remaining peak.

(1) (a) From the Ph.D. Thesis of T. J., City University of New York, 1968. (b) NSF undergraduate research participant.
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(9) R. H. Holm and F. A. Cotton, *ibid.*, **80**, 5658 (1958).
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TABLE I
GAS CHROMATOGRAPH RETENTION TIMES

Compd	Retention time, min
1,2-Epoxyoctane	7.5
2-Octenal	10.3
1-Octen-3-one	13.5
1- + 3-*t*-butyloctenyl peroxide	19.5, 21.0
1-Octen-3-ol	20.3
Peak I[a]	25.5
Peak II[b]	26.5

[a] Unidentified vpc peak from *in vacuo* reaction of *t*-butyl hydroperoxide, chromium(III) acetylacetonate, and 1-octene. [b] Unidentified vpc peak from autoxidation of 1-octene initiated by chromium(III) acetylacetonate and *t*-butyl hydroperoxide.

Autoxidation of 1-Octene by Azobisisobutyronitrile.—Following the procedure of Mayo,[8] 0.032 g of azobisisobutyronitrile was placed in 20 ml of 1-octene and permitted to absorb oxygen for 16 hr at 65–70°. Oxygen (36 ml; p = 1 atm, corrected for nitrogen evolution) was absorbed. Iodometric titration indicated formation of 0.36 mmol of hydroperoxide. Peak assignments were made on the basis of products reported by Mayo for the autoxidation of 1-hexene under similar conditions.[8]

Autoxidation of 1-Octene by Chromium(III) Acetylacetonate and *t*-Butyl Hydroperoxide.—Solutions (6 M) of 1-octene in 1-chlorooctane were autoxidized in the presence of 0.0016 M chromium(III) acetylacetonate and varying amounts of *t*-butyl hydroperoxide for several days at 30°. The reaction mixture was chromatographed as that from azobisisobutyronitrile-initiated autoxidation. After 4 days, a run at initial *t*-butyl hydroperoxide concentration of 3.3×10^{-4} M showed peroxide titration values of *ca.* 10^{-3} M.

Results and Discussion

The experimentally measured data points are of three kinds: disappearance of uv absorption at 336 mμ[9] attributed to chromium(III) acetylacetonate ($-\Delta[\mathrm{Cr}]/\Delta t$); *t*-butyl hydroperoxide decomposition ($-\Delta[t\text{-BuOOH}]/\Delta t$); and oxygen absorption ($-\Delta \mathrm{O}]_2/\Delta t$). Table II contains some initial rate data over the concentrations and temperature ranges studied. Table III gives rate "constants" and concentration superscripts of the various rate equations obtained from log–log plots of initial rates *vs.* initial concentrations. Activation parameters, Table IV, were obtained from plots of log $(\mathrm{rate}/[\mathrm{Cr}]^a[t\text{-BuOOH}]^b[\text{1-octene}]^c)_0$ *vs.* T^{-1} using the appropriate superscripts for the indicated concentration ranges.

Chromium(III) Acetylacetonate Disappearance Rates.—The chromium(III) acetylacetonate disappearance data of Tables II, III, and IV suggest a complex multistep process requiring a series of concentrations terms. The kinetics require Cr(III)–*t*-butyl hydroperoxide and Cr(III)–1-octene interaction, the conversion of Cr(III) into Cr(VI), and the production of radical species.

$$\mathrm{Cr(III)} + \nu\, t\text{-BuOOH} \rightleftharpoons \text{complex I} \quad (1)$$

$$\text{complex I} \longrightarrow \mathrm{Cr(III} + \mu) + \mu\, t\text{-BuO}\cdot + \mathrm{OH}^- \quad (2)$$

$$\mathrm{Cr(III} + \mu) + \mathrm{Cr(III)} \longrightarrow \mathrm{Cr(VI)} + \mathrm{Cr}(\mu) \quad (3)$$

$$\mathrm{Cr(III)} + \lambda \mathrm{C_8H_{16}} \rightleftharpoons \text{complex II} \quad (4)$$

$$\text{complex II} + \chi \mathrm{Z} \longrightarrow \mathrm{Cr(III} + \mu) + \mu \mathrm{Z}^- \quad (5)$$

$$-\mathrm{d[Cr]}/\mathrm{d}t = (k_1k_2/k_{-1})[\mathrm{Cr(III)}][t\text{-BuOOH}]^\nu + k_3[\mathrm{Cr(III)}][\mathrm{Cr(III} + \mu)] + (k_4k_5/k_{-4})[\mathrm{Cr(III)}][\mathrm{C_8H_{16}}]^\lambda[\mathrm{Z}]^\chi \quad (6)$$

(Z may be a reactive species such as a free radical or oxygen and Z^- represents radical and nonradical products)

The inconstancy of the superscripts and rate "constants" in the empirical expression $(\Delta[\mathrm{Cr}]/\mathrm{d}t)_0 = k[\mathrm{Cr}]^a[t\text{-BuOOH}]^b[\text{1-octene}]^c$ are evident in Table III. Values of a >1 imply that the species [Cr(III + μ)] is not a steady-state intermediate but rather some complex function of [Cr(III)] and [*t*-BuOOH]. Values of b under the conditions described in Table II are 0.5 or less, implying that steps 1 and 2 of the above scheme are fast or that the complex I need not be fully formed to react (see section on *t*-butyl hydroperoxide decomposition). The Cr(III)–1-octene complex is significant only at low *t*-butyl hydroperoxide and high 1-octene concentrations.

In the absence of oxygen or *t*-butyl hydroperoxide, there is no detectable change in the uv spectrum of chromium(III) acetylacetonate solutions in 1-octene, although identical solutions absorb oxygen (see Table II). It has been reported[11] that, in diphenyl ether, chromium(III) acetylacetonate does not absorb oxygen at 100°. This may be a solvent effect,[7] since chromium(III) acetylacetonate solutions in 1-chlorooctane absorb oxygen at 100°.[12] Direct reaction between oxygen and chromium(III) acetylacetonate is negligible in the temperature range 0–60°. Because oxygen is absorbed in the presence of 1-octene even in the initial absence of *t*-butyl hydroperoxide in the temperature range 0–60°, a 1-octene–chromium(III) acetylacetonate complex is postulated. Metal–olefin complexes are well known.[13]

The activation energy for chromium(III) acetylacetonate disappearance at low *t*-butyl hydroperoxide concentration (<0.1 M) is greater (see Table IV) than for high *t*-butyl hydroperoxide concentrations. It is also observed that at low *t*-butyl hydroperoxide concentrations the activation energy plots for chromium(III) acetylacetonate disappearance are nonlinear. Such nonlinearity might result from temperature sensitivity to the concentration of complex I, eq 1, or to the variability in structure of complex I with temperature *and* *t*-butyl hydroperoxide concentration. At higher *t*-butyl hydroperoxide concentrations, for example, more ligands might be exchanged. The generally lower activation energies for higher *t*-butyl hydroperoxide concentrations may also result from a solvent effect in which greater polarity of the medium or increased hydrogen bonding facilitates electron transfer.[14] Slightly enhanced chromium(III) acetylacetonate disappearance rates are also observed in polar solvents and in the presence of some inhibitors.[7] The positive $\Delta S^{\pm}$ values are consistent with disordering of the highly compact structure of the acetylacetonate into structures of less restricted motion.

Oxidation states of chromium between III and VI have been frequently postulated, as have reactions of Cr(IV) and Cr(V) with Cr(III) to form Cr(VI).[15] Evidence for Cr(VI) formation in this work comes from the observation that an absorption peak appears at 438 mμ as the reaction proceeds. (Dichromate is

(11) E. M. Arnett, H. Frieser and, M. A. Mendelsohn, *J. Amer. Chem. Soc.*, **84**, 2482, 3821, 3824 (1962); *J. Phys. Chem.*, **64**, 660 (1960).
(12) D. Miller, T. Jochsberger, and N. Indictor, unpublished results.
(13) P. M. Henry, *J. Amer. Chem. Soc.*, **87**, 990 (1965); R. Cramer, *ibid.*, **87**, 4717 (1965); R. J. Cventanovic, *et al.*, *ibid.*, **87**, 1827 (1965).
(14) E. Huyser in "Advances in Free Radical Chemistry," G. Williams, Ed., Logos Press, London, 1965.
(15) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, Inc., New York, N. Y., 1964, p 33 ff.

TABLE II

INITIAL RATES: DISAPPEARANCE OF *t*-BUTYL HYDROPEROXIDE;[a,b] DISAPPEARANCE OF CHROMIUM(III) ACETYLACETONATE;[a,b] OXYGEN ABSORPTION[b,c]

$[Cr(acac)_3]_0$, $\times 10^4$ M	$[t$-BuOOH$]_0$, M	$[1$-Octene$]_0$, M	Temp, °C	R_{Cr}[d]	R_P[d]	R_O[d]
4.00	0.094	2.56	−1.0[e]	0.0[f]	0.0[f]	2.03
4.00	0.76	0.64	−1.0	0.13	0.0025	n[g]
4.00	0.76	2.56	−1.0	0.31	0.0018	0.40
0.00	0.76	5.97	30		n	0.0[h]
0.762	0.00	2.56	30	0.0[i]		0.17
0.800	0.76	5.97	30	n	n	0.53
0.904	0.76	2.56	30	1.47	0.257	n
4.00	0.00	2.56	30	0.0[i]		0.34
4.00	0.00	4.50	30	0.0[i]		0.85
4.00	0.0045	2.56	30	0.39	0.0[j]	1.29
4.00	0.064	2.56	30	1.42	0.0002	n
4.00	0.094	1.27	30	n	n	2.09
4.00	0.094	2.56	30	n	0.003	2.31
4.00	0.183	0.128	30	n	n	0.90
4.00	0.76	0.00	30	2.52	1.77	0.0[k]
4.00	0.76	0.128	30	2.33	0.533	0.74
4.00	0.76	2.56	30	6.43	0.761	2.25
4.00	1.52	0.128	30	n	1.52	n
8.00	0.00	2.56	30	0.0[i]		0.57
8.00	0.76	2.56	30	13.4	0.967	n
12.00	0.094	2.56	30	n	n	5.85
0.574	0.76	2.56	40	4.27	0.565	1.15[l]
4.00	0.094	2.56	40	47.6	0.006	2.52
4.00	0.76	0.00	40	63.9	2.75	n
4.00	0.76	0.640	40	65.5	1.91	n
4.00	0.76	2.56	40	66.6	2.25	4.84
0.574	0.76	2.56	50	12.1	2.24	n
2.00	0.094	2.56	50	n	n	1.47
4.00	0.094	2.56	50	206	0.049	2.94
4.00	0.76	0.00	50	278	4.97	n
4.00	0.76	0.077	50	n	n	1.09
4.00	0.76	2.56	50	286	5.91	8.61
4.00	0.094	2.56	60	n	0.666	3.10
4.00	0.76	0.64	60	537	8.92	n
4.00	0.76	2.56	60	859	8.29	14.7
8.00	0.00	2.56	60	n		7.50

[a] *In vacuo.* [b] Reactions run in 1-chlorooctane. [c] Oxygen pressure = 1 atm. [d] $R_{Cr} = (-\Delta[Cr(acac)_3]/\Delta t)_0 \times 10^{-9}$ M/sec; $R_P = (-\Delta[t$-BuOOH$]/\Delta t)_0 \times 10^{-4}$ M/sec; $R_O = (-\Delta[O_2]/\Delta t)_0 \times 10^{-6}$ M/sec. [e] Autoxidations run at 2°. [f] No detectable change after 15 days. [g] n = no data. [h] No oxygen picked up for 5.5 hr. [i] No detectable change after 18 hr. [j] No detectable change after 71 hr. [k] Negligible oxygen pick-up (< 1 ml) after 7 hr. [l] $[Cr(acac)_3]_0 = 8.0 \times 10^{-5}$ M.

known to have an absorption at 440 mμ.)[16] It is also observed that as the reaction proceeds (in 1-chlorooctane in either the presence or absence of oxygen) the initially pale purple solution takes on a yellow-orange color suggestive of chromate or dichromate. In the presence of a few drops of methanol, the characteristic blue color of chromium peroxides[17] is developed instead of the yellow-orange color. A similar blue color is obtained by adding potassium dichromate to a solution of *t*-butyl hydroperoxide and 1-octene in methanol.

The Decomposition of *t*-Butyl Hydroperoxide.—Initial rates, empirical kinetic equations, and activation parameters for *t*-butyl hydroperoxide decomposition *in vacuo* are listed in Tables II, III, and IV.

The activation parameters in Table IV indicate a process consistent with O–O bond rupture at low *t*-butyl hydroperoxide concentrations. The entire effect of the presence of chromium(III) acetylacetonate upon the decomposition process is in the entropy term, implying that the chromium species serves as a favorable site for bond rupture. When *t*-butyl hydroperoxide is present in higher concentrations (>0.1 M), the activation enthalpy is *ca.* 20 kcal/mol, consistent with a chain process for decomposition in which some decomposition occurs at chromium sites and some by induced decomposition by radicals generated from the initiation process. Inhibitor studies also support chain decomposition of *t*-butyl hydroperoxide.[7]

For *t*-butyl hydroperoxide concentrations >0.1 M, chain decomposition in which most of the *t*-butyl hydroperoxide disappears in the propagation step is consistent with initiation by chromium(III) acetylacetonate disappearance. Assuming steady-state conditions

$$-d[t\text{-BuOOH}]/dt = k_p[t\text{-BuOOH}][R\cdot] \quad (7)$$

R· = *t*-BuO·, *t*-BuOO·, and octenyl radicals

$$-d[t\text{-BuOOH}]/dt \propto (k_p/k_t^{1/2})R_i^{1/2} \quad (8)$$

(16) H. H. Willard, L. L. Merritt, Jr., and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1963, p 133.

(17) T. Moeller, "Inorganic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1961, p 514.

TABLE III

EMPIRICAL RATE EQUATIONS

$[Cr]_0$,[a] $\times 10^4$ M	$[t\text{-BuOOH}]_0$, M	$[1\text{-Octene}]_0$, M	Temp, °C	$k \times 10^4$	a	b	c
A. $\left(\frac{-\Delta[Cr]}{\Delta t}\right)_0 = k[Cr]_0^a[t\text{-BuOOH}]_0^b[1\text{-Octene}]_0^c$							
4.0–16.0	0.8	2.56	−1.0	0.0005	1.0	n[b]	n
4.0	0.8	0.6	30	0.067	n	n	0.0
0.8–8.0	0.005–0.8	0.6–2.6	30	0.072	1.0	0.52	1
0.6–4.0	0.1–0.8	0.6–2.6	40	0.282	1.4	0.13	0.0
0.6–4.0	0.1–0.8	0.6–2.6	50	1.12	1.7	0.13	0.0
B. $\left(\frac{-\Delta[t\text{-BuOOH}]}{\Delta t}\right)_0 = k[Cr]_0^a[t\text{-BuOOH}]_0^b[1\text{-Octene}]_0^c$							
4.0	0.005–0.8	2.6	30	1.59	n	$1 < b < 4$	n
0.9–4.0	0.8–1.6	0.13–2.6	30	50.1	0.49	1.0	0.0
0.6–4.0	0.1–8.0	0–2.6	40	138	0.71	2.9	0.0
0.6–4.0	0.1–8.0	0–2.6	50	407	0.50	2.3	0.0
C. $\left(\frac{-\Delta[O_2]}{\Delta t}\right)_0 = k[Cr]_0^a[t\text{-BuOOH}]_0^b[1\text{-Octene}]_0^c$							
4.0	0.09–0.8	2.6	2	6.03	n	−0.7	n
4.0–12.0	0.0004–0.02	0.13–4.5	30	40.1	0.85	0.49	0.23
4.0	0.8	0.07–2.6	30	146	n	n	0.93
0.8–8.0	0.1–0.8	2.6	30	41.3	1.1	0.0	0.26
4.0	0.1–4.5	0.13	30	22.5	n	−0.2	n
0.8–8.0	0.0	2.6–6.0	30	0.049	0.45		1.57
4.0	0.02–0.09	2.6	40	42.4	n	0.16	n
0.8–4.0	0.8	2.6	40	97.0	1.0	n	n
4.0	0.8	0.07–0.26	40	214	n	n	0.95
4.0	0.8	0.07–0.26	50	324	n	n	0.76
2.0–4.0	0.1–0.8	2.6	50	180	1.1	0.51	n
4.0	0.1–0.8	2.6	59	326	n	0.77	n

[a] Cr = Chromium(III) acetylacetonate. [b] n = no data.

TABLE IV

ACTIVATION PARAMETERS[a]

$[Cr]_0$,[b] $\times 10^4$ M	$[t\text{-BuOOH}]_0$, M	$[1\text{-Octene}]_0$, M	E_{act}, kcal/mol	$\Delta S^{\ddagger}$, cal/deg-mol	$\Delta H^{\ddagger}$, kcal/mol
A. Disappearance of Cr[b,c]					
4.00	0.76	2.56	26.6 ± 3.5	3.32	26.0
4.00	0.093	2.56	(30–46)[d]	(41.8)[d]	(37.8)[d]
4.00	0.76	0.00	39.3 ± 2.8	45.2	38.7
4.00	0.76	0.64	29.1 ± 5.6	11.1	28.5
B. Decomposition of t-BuOOH[c]					
4.00	0.76	2.56	19.9 ± 4.1	−5.72	19.3
4.00	0.093	2.56	41.7 ± 8.4	66.5	41.1
4.00	0.76	0.00	10.1 ± 1.7	−36.4	9.5
4.00	0.76	0.64	20.2 ± 4.0	−5.04	19.6
C. Autoxidation of 1-Octene[e]					
4.00	0.76	2.56	12.1 ± 0.7	−31.8	11.5
4.00	0.093	2.56	1.3 ± 0.1	−67.8	0.66
4.00	0.76	0.256	7.66 ± 0.43	−44.2	7.05
4.00	0.76	0.077	7.5 ± 0.16	−44.2	6.93
4.00	0.00	2.56	18.2 ± 0.3	−11.4	17.3

[a] Temperature range = −1.0–60° for A and B and 2–59° for C. [b] Cr = Chromium(III) acetylacetonate. [c] *In vacuo*, 1-chlorooctane solvent. [d] Nonlinear Arrhenius plot. [e] 1-Chlorooctane solvent, oxygen pressure = 1 atm.

where k_t = termination rate constant and R_i = initiation rate = $f([Cr], [t\text{-BuOOH}], [1\text{-octene}])$, *e.g.*, eq 6.

$$E_{obsd} = E_p - 0.5\,E_t + 0.5\,E_i \quad (9)$$

E_{obsd} = observed activation energy
E_p = activation energy for propagation, eq 7
E_t = activation energy for termination
E_i = activation energy for the initiation process

Calculated values of E_p, assuming that $E_t \cong 0$–2 kcal/mol[18] and E_i is identical with the activation energy for chromium(III) acetylacetonate disappearance give E_p = 6.6–7.6 kcal/mol, in good agreement with literature values of 7.0–7.5 kcal/mol.[19]

In the absence of olefin, the low activation energy for t-butyl hydroperoxide disappearance cannot be consistent with initiation rates from chromium(III) acetylacetonate disappearance unless an unusually large activation energy for termination is postulated. It is more likely that a much lower activation energy, 3–5 kcal/mol, for initiation perhaps involving ligand

(18) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 95.

(19) S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1960).

exchange[20] occurs before the experimentally observed chromium(III) acetylacetonate disappearance.

The effect of 1-octene on *t*-butyl hydroperoxide rates is generally consistent with the behavior of a weak inhibitor or chain transfer agent. At 30°, the chromium(III) acetylacetonate induced decomposition of *t*-butyl hydroperoxide in 1-chlorooctane is decreased by the presence of 1-octene. This effect is less as temperature rises. At 50°, 1-octene has a small accelerating effect upon the rate. This effect is understandable in terms of differences in activation energy for propagation and termination involving octenyl radicals. Termination is less sensitive, generally, to temperature than hydrogen abstraction processes,[21] and weak inhibitors (or retarders) at low temperatures may show opposite effects at increased temperatures. It has frequently been found that a series of solvent–hydroperoxide or olefin–hydroperoxide terms is required to describe the kinetic behavior of hydroperoxide decomposition data.[21-23] The accelerating effects of these interactions are undoubtedly sensitive to temperature.

Autoxidations.—Initial oxygen absorption rates, empirical kinetic equations, and activation parameters for the autoxidation of 1-octene with chromium(III) acetylacetonate and *t*-butyl hydroperoxide are listed in Tables II, III, and IV. The multiplicity of rate laws and activation parameters again implies a complex multistep process.

A clearly detectable autoxidation is discernible in the absence of *t*-butyl hydroperoxide which shows a markedly higher activation energy than autoxidation in the presence of *t*-butyl hydroperoxide. This process, which probably involves 1-octene–chromium(III) acetylacetonate interactions, would be more important at higher temperatures.

At low hydroperoxide concentration (<0.1 *M*), autoxidation has a very low activation energy and a very low entropy of activation consistent, in the usual processes, eq 9, with low activation energy initiation or high energy termination. Important propagation steps would be

$$C_5H_{11}\underset{\underset{O_2\cdot}{|}}{C}HCH{=}CH_2 + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow C_5H_{11}\underset{\underset{O_2H}{|}}{C}H{=}CH_2 + C_5H_{11}\underset{\underset{O_2H}{|}}{C}HCH{=}CH_2 \quad (10)$$

$$t\text{-BuO}\cdot \text{ or } t\text{-BuOO}\cdot + C_5H_{11}CH_2CH{=}CH_2 \longrightarrow t\text{-BuOH or } t\text{-BuOOH} + C_5H_{11}\underset{\underset{O_2H}{|}}{C}HCH{=}CH_2 \quad (11)$$

with significant chain transfer.[15]

$$C_5H_{11}\underset{\underset{O_2\cdot}{|}}{C}HCH{=}CH_2 + t\text{-BuOOH} \longrightarrow C_5H_{11}\underset{\underset{O_2H}{|}}{C}HCH{=}CH_2 + t\text{-BuOO}\cdot \quad (12)$$

If it is assumed that peroxy radical coupling reactions lead to termination ($E_t \cong 10$ kcal/mol)[24] and eq 10–12 are important propagation steps ($E_p \cong 7$ kcal/mol),[19] then the observed activation energy should be about half the activation energy of the initiation process (within *ca.* ± 5 kcal/mol). It may be seen from inspection of Table IV that at low *t*-butyl hydroperoxide concentrations (<0.1 *M*) the initiation process cannot be interpreted either in terms of *t*-butyl hydroperoxide decomposition or chromium(III) acetylacetonate disappearance, but must involve complex formation not kinetically detectable in our system. At *t*-butyl hydroperoxide concentrations >0.1 *M*, activation parameters for autoxidation are obtained consistent with chromium(III) acetylacetonate disappearance rates as a measure of the initiation process.

It is clear from the activation parameters and the complex kinetic equations that neither *t*-butyl hydroperoxide decompositions nor autoxidations in the presence of chromium(III) acetylacetonate obey the relatively simple schemes postulated for these types of reactions.[25-28] Both types of reactions are chain reactions, although the initiation processes do not correspond to chromium(III) acetylacetonate disappearance rates at low (<0.1 *M*) *t*-butyl hydroperoxide concentrations. Table V lists ratios $(\Delta[O_2]/\Delta[Cr])_0$ and $([\Delta[t\text{-BuOOH}]/\Delta[Cr])_0$ from initial rate data. These numbers represent chain lengths for *t*-butyl hydroperoxide concentrations >0.1 *M* and probably indicate a rough estimate of chain length for *t*-butyl hydroperoxide concentrations <0.1 *M*. It is observed that longer chains are achieved at lower initial chromium(III) acetylacetonate concentrations and lower temperatures.

TABLE V

OBSERVED RATE RATIOS OF OXYGEN ABSORPTION AND *t*-BUTYL HYDROPEROXIDE DISAPPEARANCE COMPARED WITH CHROMIUM(III) ACETYLACETONATE DISAPPEARANCE.

$[Cr(acac)_3]_0$, × 10⁴ *M*	$[t\text{-BuOOH}]_0$, *M*	$[1\text{-Octene}]_0$, *M*	Temp, °C	R_0/R_{Cr}	R_p/R_{Cr}
4.00	0.76	2.56	−1.0	1300	580
0.904	0.76	2.56	30	350	18000
4.00	0.0047	2.56	30	2700	0[a]
4.00	0.064	2.56	30	n[b]	14
4.00	0.094	2.56	30	1000	130
4.00	0.76	0.128	30	320	23000
4.00	0.76	0.640	30	600	n
4.00	0.76	2.56	30	350	12000
8.00	0.76	2.56	30	340	7200
0.574	0.76	2.56	40	190	13000
4.00	0.094	2.56	40	53	13
4.00	0.76	0.64	40	n	2900
4.00	0.76	2.56	40	73	3400
0.574	0.76	2.56	50	n	19000
4.00	0.094	2.56	50	14	24
4.00	0.76	0.64	50	n	1800
4.00	0.76	2.56	50	30	2100
4.00	0.76	0.64	60	n	1700
4.00	0.76	2.56	60	17	970

[a] No detectable *t*-BuOOH decomposition after 71 hr. However, the rate is probably not zero; a rate of 10^{-9} *M*/sec would be beyond the limits of detection but would result in a value of about one for the chain length. [b] n = no data.

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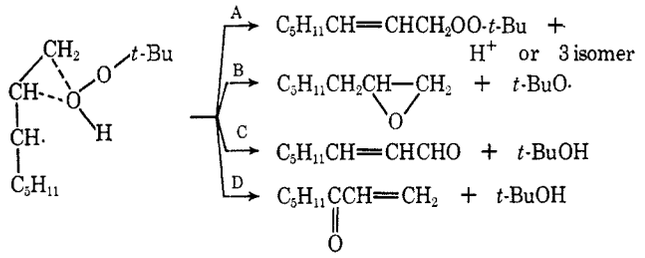
TABLE VI

AUTOXIDATION PRODUCTS

	mmol of product obtained/mmol of O_2 consumed under the following conditions			
	1-Hexene (384 mmol),[a] 8.92 × 10^{-3} *M* ABC initiator, 90°, 753 min, 40 psc O_2, 18.1 mmol of O_2 consumed	1-Octene (128 mmol), 9.75 × 10^{-3} *M* AIBN initiator, 70°, 945 min, 15 psc O_2, 1.61 mmol of O_2 consumed	1-Octene (6.4 *M*), 1.6 × 10^{-3} *M* Cr(acac)$_3$, 0.095 *M* *t*-BuOOH, 30°, 7 days, 15 psc O_2, 0.67 mmol of O_2 consumed	1-Octene (6.4 *M*), 1.6 × 10^{-3} *M* Cr(acac)$_3$, 0.76 *M* *t*-BuOOH, 30°, 1 day, 15 psc O_2, 2.85 mmol of O_2 consumed
Hydroperoxide[b]	0.258	0.225	...	...
Alcohol[b]	0.033	0.147	...	...
Ketone	0.042	0.138	0.644	0.752
Aldehyde	0.040	0.118	0.040	0.171
Epoxide	0.048	0.042	0.029	0.033
Residue	0.324			0.234
Peak II (Table I)			0.439	0.145

[a] Reference 8. [b] May be mixtures of isomers.

Products. Absence of Oxygen.—When *t*-butyl hydroperoxide, chromium(III) acetylacetonate, and 1-octene were allowed to react for 10 days at 30° in the absence of oxygen, *t*-butyl alcohol, 1,2-epoxyoctane, 2-octenal, 1-octen-3-one, and an unidentified substance of high molecular weight (*ca.* two C_8 units) were detected (peak I, Table I) gas chromatographically. The experiment was repeated with cuprous chloride instead of chromium(III) acetylacetonate for 5–6 hr at 60–70° according to the method of Kharasch and Fono,[10] and the reaction mixture was analyzed under the same gas chromatographic conditions as that from experiment using chromium(III) acetylacetonate. Only 2-octenal was common to both reaction mixtures. Kharasch and Fono suggest the intermediacy of a radical peroxide complex such as that shown. This complex is oxidized mainly to dialkyl peroxide (path A) in the presence of copper, but paths B, C, and D are available when chromium(III) acetylacetonate is



present, apparently to the exclusion of path A, implying that, if this reaction takes place at ligand sites, *t*-butyl hydroperoxide has a greater affinity for chromium than it does for the 1-octene or for the copper. No ketone peak was found in the presence of cuprous chloride, and no dialkyl peroxide peak was found in the presence of chromium(III) acetylacetonate. These experiments established that the chromium(III) acetylacetonate catalyzed reaction is not identical with the cuprous chloride catalyzed reaction.

Products. Presence of Oxygen.—When 1-octene is autoxidized in the presence of chromium(III) acetylacetonate and *t*-butyl hydroperoxide, the main products as determined by gas chromatography are *t*-butyl alcohol, 1-octen-3-one, 1,2-epoxyoctane, an unidentified substance (*ca.* two C_8 units, peak II, Table I), and residue (more than two C_8 units) and octenyl hydro peroxide (by iodometric titration).

Products of the autoxidation of 1-octene chromatographically observed at different initial *t*-butyl hydroperoxide concentrations at 30° are listed in Table VI side by side with product distributions obtained by Mayo, *et al.*,[8] from the azobiscyclohexane-1-carbonitrile initiated autoxidation of 1-hexene at 90° and in this laboratory from the azobisisobutyronitrile autoxidation of 1-octene at 65–70°. Mayo actually converted hydroperoxide formed to alcohol with triphenylphosphine and corrected the chromatographically obtained values.[8] In this laboratory, products were chromatographed directly. All peaks could be accounted for without assigning one to octenyl hydroperoxide. Under our chromatographic conditions, octenyl hydroperoxide was probably converted into ketone, alcohol, and aldehyde, in which case close correspondence is obtained between Mayo's data for 1-hexene and our data for 1-octene. The chromium(III) acetylacetonate–*t*-butyl hydroperoxide initiated runs differ in showing no alcohol and higher yields of 1-octen-3-one, arising partly from octenyl hydroperoxide decomposition and partly from the direct attack of *t*-butyl hydroperoxide upon 1-octene in the presence of chromium(III) acetylacetonate (see preceding section). The absence of alcohol may result from rapid oxidation by a chromium species.[15] When methanol was used as a solvent,[7] enough formaldehyde was produced to make the measured autoxidation rate appear to be negligible.

Registry No.—1-Octene, 111-66-0; *t*-butyl hydroperoxide, 75-91-2; chromium(III) acetylacetonate, 13681-82-8.

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